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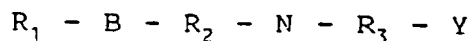
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(54) **Amphoteric surfactants having multiple hydrophobic and hydrophilic groups**

(57) According to the invention, an improved class of amphoteric surfactant having improved surfactant properties characterized as mild and environmentally safe has been provided comprising compounds of the formula:



I.

R_4



The amphoteric surfactant of the subject invention have at least two hydrophobic moieties and at least two hydrophilic groups per molecule and are useful as emulsifiers, detergents, dispersants and solubilizing agents.

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Description

This invention relates to a novel group of amphoteric surfactants having at least two hydrophobic moieties and at least two hydrophilic groups per molecule useful as emulsifiers, detergents, dispersants, hydrotropes, wetting agents, corrosion inhibitors and solubilizing agents.

BACKGROUND OF THE INVENTION

Surfactants are well known materials which can be generally described as having a hydrophobic moiety and a hydrophilic group per molecule. A variety of these materials are known and are classified as anionic, cationic, nonionic and amphoteric. They are well known to be useful as emulsifiers, detergents, dispersants and solubilizing agents in the fields of cosmetics, textile treatment, industrial and personal cleaning preparations, corrosion inhibitors and the like.

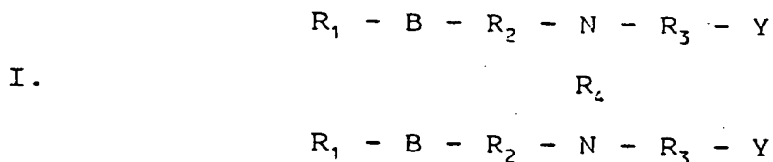
In many surfactant containing compositions, such as personal cleaning preparations, mildness is a sought after characteristic. The amphoteric surfactants are particularly important in fulfilling that need. Amphoteric surfactants are compounds uniquely structured to function as cationic surfactants at acid pH and anionic surfactants at alkaline pH. At neutral pH, the amphoteric surfactants are neutral thus accounting for their mildness. These compounds are well known and some of these are shown in U.S. Pat. Nos. 3,941,817; 4,705,843; 2,781,354 and 2,773,068 which are illustrative. Amphoteric surfactants are also known to be biodegradable, hence are ecologically compatible.

Surfactants generally are compounds having one hydrophilic group and one hydrophobic moiety. Recently, a group of compounds having two hydrophobic moieties and two hydrophilic groups have been introduced. These have become known as "Gemini surfactants" in the literature [*Chemtech*, March 1993, pp 30 - 33, -], and *J. American Chemical Soc.*, 115, 10083-10090, (1993) and the references cited therein. Since their introduction, cationic and anionic "Gemini surfactants" have been disclosed. Other surfactant compounds having two hydrophilic groups and two hydrophobic moieties have been disclosed but not referred to as Gemini surfactants.

Due to the need for new and more effective and efficient surfactants, as well as the need for mild surfactants which are biologically compatible in an ecologically sensitive environment, effort has been made to develop a new class of compounds, which demonstrate improved surface-active properties that are further characterized as mild, and environmentally benign.

SUMMARY OF THE INVENTION

According to the invention, an improved class of amphoteric surfactants having improved surfactant properties characterized as mild and environmentally benign has been provided comprising compounds of the formula:



wherein R_1 can independently be C_5 to about C_{22} alkyl or the hydroxy substituted or perfluorinated derivatives thereof, R_2 can independently be C_1 to about C_{12} alkylene or hydroxy substituted alkylene; B can be an amide group $[-C(O)N(R_5)-$ or $-N(R_5)C(O)-]$, a carboxyl group $[-C(O)-O-$ or $-OC(O)-]$ or a polyether group $[-O(R_6-O)_x-]$, wherein R_5 independently represents lower alkyl or hydroxy substituted alkyl from 1 to about 4 carbons or hydrogen and R_6 independently represents about C_2 to about C_4 alkyl with x being a number between 1 and 20; R_3 can independently be C_1 to about C_{10} alkylene and the hydroxy substituted derivatives thereof or R_7-D-R_7 or a polyether group $[-O(R_6-O)_x-]$, wherein R_6 is as defined hereinbefore and R_7 can independently be C_1 to about C_6 alkylene and the hydroxy substituted derivatives thereof or R_7-D-R_7 , or a polyether group and D represents $-O-$, $-S-$ or $-N(R_8)-$ wherein R_8 independently represents C_1 to about C_{12} alkyl and the hydroxy substituted derivatives thereof or hydrogen; R_4 can independently be alkylene or alkylaryl of 1 to about 10 carbon atoms and the hydroxy substituted derivatives thereof or $R_9-D_1-R_9$ wherein R_9 can independently be alkylene of from 1 to about 6 carbon atoms and the hydroxy substituted derivatives thereof as well as aryl illustrated by phenylene, diphenylene and sulphonyldiphenylene, and D_1 represents $-O-$, $-S-$, $-SO_2-$, a carbonyl group, a polyether group $[-O(R_6-O)_x-]$, $(R_{10})_y(N(R_{10}))_z$ or aryl wherein R_{10} represents alkyl of from 1 to about 12 carbon atoms and the hydroxy substituted derivatives thereof or hydrogen, R_6 being as defined hereinbefore with x being a number between 1 and 20 and y and z are independently numbers from 1 to about 4; and Y independently represents $-SO_3H$, $-OSO_3H$, $-OP(O)(OH)_2$, $-P(O)(OH)_2$, $-COOH$, $-CO_2-C_6H_4-SO_3H$ and salts thereof.

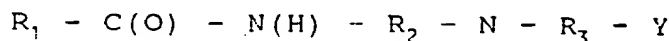
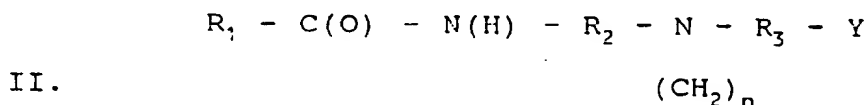
Preferably, R_1 is alkyl or perfluoroalkyl of from about C_6 to about C_{18} carbon atoms. R_2 is preferably alkylene of

from about C₂ to about C₆ carbon atoms. B is preferably an amide group. Preferably, R₃ is independently lower alkyl ne of from 1 to about 4 carbon atoms and the hydroxy substituted derivatives thereof. R₄ is preferably lower alkylene and the hydroxy substituted derivatives thereof of from 1 to 10 carbon atoms. Y is preferably carboxy, sulfate, phosphate and salts thereof.

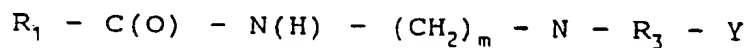
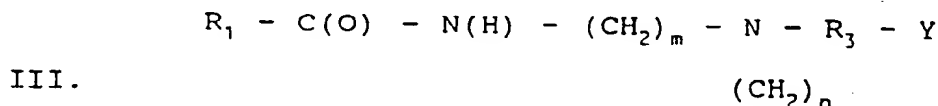
When compared to the corresponding conventional amphoteric surfactants of the lauryl amphopropionate and coco amphosulfonate types, the novel compound of the invention show two unexpected surface active properties; unusually low critical micelle concentration (CMC) and pC-20 values in aqueous media. These properties are a measure of the tendency of the surfactant to form micelles and adsorb at the interface respectfully, and consequently, to reduce surface tension.

The salts of Formula I can be an alkali metal salt (Na, K), an alkaline earth metal salt (Mg, Ca), an ammonium salt, or an organic base salt. The organic base salt can be illustrated by monoethanolamine, diethanolamine, triethanolamine, triethylamine, trimethylamine, N-hydroxyethyl morpholine and the like.

Preferably, the compounds of the present invention comprise:

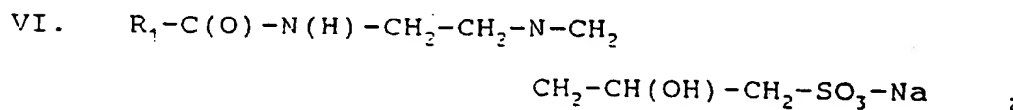
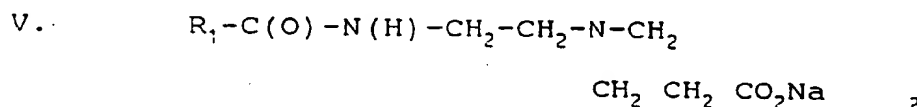
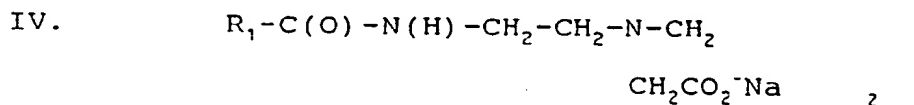


more particularly, the compounds of the invention comprise:



wherein R₁, R₂, R₃, and Y are as defined hereinbefore, n equals a number of between about 2 to about 10, and m equals a number between about 2 and about 10.

Representative compounds within the invention include:



In addition to new compounds, the invention also provides novel methods of preparing the same as well as synergistic compositions when blended with other surfactants.

DETAILED DESCRIPTION OF THE INVENTION

In the compounds of the above formulae, R₁ is derived from fatty acids from natural or synthetic sources and generally will contain mixtures of different carbon chain length radicals within the chain length ranges defined above. R₁

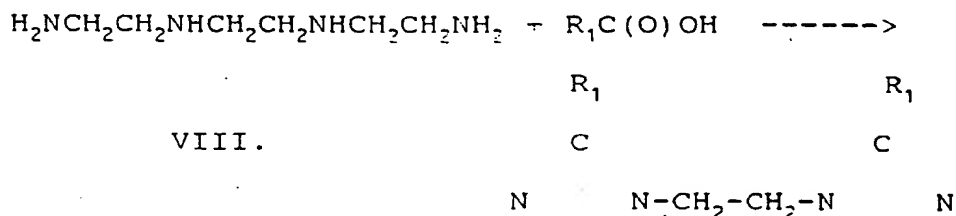
can be a mixture of saturated and unsaturated aliphatic radicals. The natural sources can be illustrated by coconut oil or similar natural oil sources such as palm kernel oil, palm oil, soya oil, rapeseed oil, castor oil or animal fat sources such as herring oil and b l tallow. Each R from natural sources can be a mixture of alkyl radicals containing from about 5 to about 22 carbon atoms. In a more preferred material, the mixture of alkyl radicals can be derived from a saturated portion of coconut oil or similar natural vegetable oil. In the case of coconut oil fatty acid, each R ranges from about 6 to about 18 carbon atoms. These ranges are given as covering about 90% of the R groups, i.e., carbon chains, in the compound. Since these R groups are derived from natural sources, they can contain small amounts of other carbon chains. Illustrative of the fatty acids in these oils are caprylic(C₈), capric(10), lauric (12), myristic(14) palmitic(16), stearic (18), oleic (18, monounsaturated), linoleic (18, diunsaturated), linolenic (18, triunsaturated), ricinoleic (18, monounsaturated), arachidic (20), gadolic(20, monounsaturated), behenic (22) and erucic(22). These fatty acids can be used per se, as concentrated cuts or as fractionations of natural source acids. The even numbered acids are given as illustrative though the odd numbered fatty acids can also be used. In addition, amphoteric, based on single carboxylic acids, e.g., lauric acid, or other cuts, as suited for the particular application, may be used. Examples of useful acids derived from synthetic sources are 2-ethylhexanoic acid, pelargonic acid and the like.

While the compounds of the present invention can be prepared by a variety of synthetic routes, it has been found that they can be produced particularly effectively by a novel process which utilizes a polyamine reactant having at least four amino groups of which two are terminal primary amines. The preferred polyamine can be illustrated by triethylene tetramine (TETA). Other polyamines such as tetraethylenepentamine and others can also be used. The amine reactant can be defined by the structure:

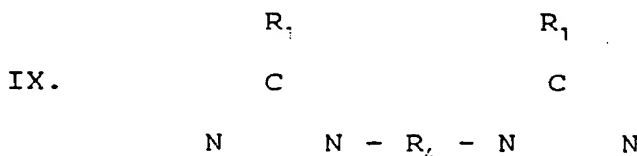


wherein R₄ is generally alkyl or aminoalkyl. The improved method of the invention will be illustrated with TETA but this is not intended to limit the invention to that starting material.

TETA is reacted with a fatty acid or ester or triglyceride to form a bisimidazoline as per the equation:



This compound can be generically defined by the structure:



The fatty acids, esters or triglycerides thereof can be reacted with the polyamines at temperatures ranging from about 150° to 250°C with continuous removal of the resulting condensate (H₂O). The process can be carried out with excess amine, with or without a catalyst, at atmospheric, reduced or super atmospheric pressure.

The bisimidazoline compound, when hydrolyzed under basic pH conditions will selectively form a bisamidoamine compound of Formula X:



This compound can be generically represented by compounds of the formula:



The bisamidoamine compound (Compounds of Formula X or XI) can then be reacted with an alkylating agent to prepare the bisamphoteric compounds of the invention as defined in Formula I such as an organic compound with a r active halogen illustrated by chloroacetic acid, its esters or salts; an activ vinyl compound, which undergo s Micha l addition, illustrated by methyl acrylate or sodium vinyl sulfonate; or electrophiles such as propane sultone or sodium, 3-chloro-2-hydroxypropyl sulfonate and the like.

For alkylation conditions and commonly used alkylating agents, see Amphoteric Surfactants Vol. 12, Ed. B.R.

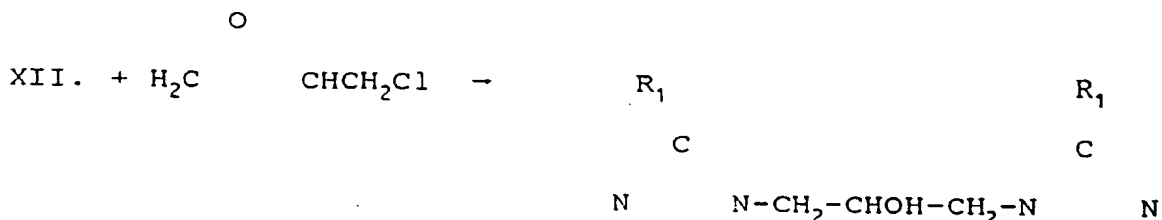
Bluestein and C.L. Hilton, Surfactant Science Series 1982, pg. 17 and references cited therein, the disclosures of which are incorporated herein by reference.

A second mode of synthesis from ethylenediamine and a fatty acid can be shown by the following equation:



The fatty acids or esters or triglycerides thereof can be reacted with α, β - diamines at temperatures ranging from about 150° to 250°C with continuous removal of the resulting condensate (H_2O). The process can be carried out with excess amine, with or without a catalyst, at atmospheric, reduced or super atmospheric pressure.

The imidazoline as represented by Formula XII can then be reacted with any difunctional compound that will join two of the imidazoline rings to form the bisimidazoline compound as represented by Formula X. These can be illustrated by any reactive dihalide, e.g., alpha, omega-dihaloethane, alpha, beta-dihaloethane, alpha, alpha'-dihaloethane, diglycidyl ethers, diepoxides as well as epichlorohydrins such as epichlorohydrin and the like.



XIII.

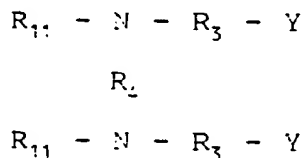
In addition to the groups above in connection with the polyamine, R_4 can be illustrated by hydroxy substituted alkyl such as $-CH_2CHOHCH_2-$; an ether such as $-CH_2CH_2OCH_2CH_2-$ or an alkylarylalkyl such as $CH_2C_6H_4CH_2-$.

For reaction conditions generally, see JACS 67, 1581(1945); US 1,790,042; 1,845,403; JCS 1666 (1931), the disclosures of which are incorporated herein by reference.

The bisimidazoline compound represented by Formula XIII like the bisimidazoline compound represented by Formula VIII as discussed hereinbefore, when hydrolyzed under basic pH conditions will form the amidoamine compound as represented by Formula XI where R_4 is $-CH_2CH(OH)CH_2-$ which can be reacted with an alkylating agent to form the bisamphoteric compounds represented by Formula I.

The surfactants of the invention can be used alone as the essential hydrotrope component.

It has also been unexpectedly found that blends of the compounds of the invention as defined by the formula



wherein R_{11} can independently be alkyl or hydroxy alkyl of from 5 to 22 carbons or $R_1 - B - R_2$ wherein R_1 , R_2 , R_3 , and R_4 are as defined hereinbefore with certain conventional well known anionic, nonionic, cationic and amphoteric surfactants provide synergistic results that can be demonstrated in relation to critical micelle concentration and surface tension reducing ability.

Examples of the nonionic surfactants used herein include fatty acid glycerine esters, sorbitan fatty acid esters, sucrose fatty acid esters, polyglycerin fatty acid esters, higher alcohol ethylene oxide adducts, single long chain polyoxyethylene alkyl ethers, polyoxyethylene alkyl aryl ethers, polyoxyethylene lanolin alcohol, polyoxyethylene fatty acid esters, polyoxyethylene glycerine fatty acid esters, polyoxyethylene propyl n glycol fatty acid esters, polyoxyethylene sorbitol fatty acid esters, polyoxyethylene castor oil or hardened castor oil derivatives, polyoxyethylene lanolin derivatives, polyoxyethylene fatty acid amides, polyoxyethylene alkyl amines, an alkylpyrrolidone, glucamides, alkylpolyglu-

cosides, mono- and dialkanol amides, a polyoxyethylene alcohol mono- or diamides and alkylamine oxides. Examples of the anionic surfactants used herein include fatty acid soaps, ether carboxylic acids and salts thereof, alkane sulfonate salts, α -olfin sulfonate salts, sulfonate salts of higher fatty acid esters, higher alcohol sulfate ester salts, fatty alcohol ether sulfates salts, higher alcohol phosphate ester salts, fatty alcohol ether phosphate ester salts, condensates of higher fatty acids and amino acids, and collagen hydrolysate derivatives. Examples of the cationic surfactants used herein include alkyltrimethylammonium salts, dialkyldimethylammonium salts, alkyldimethylbenzylammonium salts, alkylpyridinium salts, alkylisoquinolinium salts, benzethonium chloride, and acylamino acid type cationic surfactants. Examples of the amphoteric surfactants used herein include amino acid, betaine, sultaine, phosphobetaines, imidazoline type amphoteric surfactants, soybean phospholipid, and yolk lecithin.

In addition to the foregoing surfactants, any of the commonly used auxiliary additives may be added to the surfactants of the invention or blends thereof with other surfactants as disclosed herein. Such auxiliary additives may be suitably chosen for a desired composition and generally include inorganic salts such as Glauber salt and common salt, builders, humectants, solubilizing agents, UV absorbers, softeners, chelating agents, and viscosity modifiers.

The amphoteric surfactants of the present invention exhibiting greater surface tension reduction, low toxicity, and excellent compatibility with other anionic, cationic and nonionic surfactants, and being extremely mild and non-irritating to both eyes and skin as well are adaptable for use in products ranging from cosmetics to industrial applications and are usable wherever amphoteric surfactants have found use.

These products are particularly useful for non-irritating shampoos including baby shampoos, body shampoos including bubble baths, bar soaps, bath gels, hair conditioning gels, lotions, skin creams and lotions, make up removal creams and lotions, liquid detergents, dish detergents and other washing and cosmetic products that contact the skin as well as bleach activators and bleach stabilizers and the like.

In addition, the compounds and compositions of the invention can be used in connection with hard surface cleaners, high electrolyte cleaners, emulsion polymerization, liquid and bar soap, laundry and dish detergents, bottle washing, carpet shampoo, water based lubricants, metal cleaning, wax softener, oil well drilling lubricant and the like.

Examples of the present invention are given below by way of illustration and not by way of limitation. All parts and percents are by weight.

EXAMPLE 1

Synthesis of Ethylene bis-laurimidazoline of Formula VIII where R1 is C11H23.

To a 500 mL, three-necked, round bottom flask equipped with a stirrer, temperature controller, and a Barrett distilling receiver with a condenser on top, was added 46.7 g (0.25 mol) triethylenetetramine hydrate (average 2.1 to 2.2 moles water by Karl Fisher Analysis), 104 g (0.52 mol) lauric acid and 100 mL toluene. The Barrett distilling receiver was filled with toluene. The reaction mixture was gently heated with stirring to reflux (120° - 130°C) and water collection was initiated.

The progress of the reaction was followed by monitoring the amount of water collected as the toluene azeotrope. The first 20 mL which was collected in the first three hours of the reflux period indicated that the reaction was 70% complete.

The reaction temperature was slowly raised to 160° - 180°C during the 12 to 16th hour of reaction by stripping the reactor-contained toluene through the Barrett distillation receiver. The progress of the reaction was also determined by gas chromatography. The disappearance of the peak corresponding to the diamide indicated completion of the condensation reaction.

After 16 hours of reaction, the reaction was stopped, as 27.2 mL (99% of the theoretical 28 mL) of water had been collected. Gas chromatography showed that the 126 grams of product obtained contained greater than 96% of the desired ethylene bis-laurimidazoline (VIII).

The product was recrystallized from CHCl_3 for structure characterization and identification. The ^1H and ^{13}C NMR, IR, and Mass Spectra were recorded and the results agreed with the postulated structure.

EXAMPLE 2

Synthesis of N N'- bis(2-lauramidoethyl) ethylenediamine of Formula X wherein R1 is C11H23.

To a 100 mL three-necked round bottom flask equipped with magnetic stirrer-bar, temperature control, a condenser and a pH probe connected with a readout, was added a solution of 0.2 g of NaOH in 2 mL water and 4.74 g (10 mmol) of ethylene bis-laurimidazoline prepared by the process in Example 1. The reaction mixture was then stirred, heated and maintained at 85-95°C for 6-8 hours until the pH value of the reaction mixture remained unchanged. Analysis by gas chromatography indicated less than 5% of the starting material (some of the starting material shown by GC is caused

by cyclization of the compound of Formula IX in GC injection port). The reaction was stopped at this point to avoid further hydrolysis of the desired bisamidoamine compound of Formula X. The mixture was cooled to 60°C and diluted with 2 mL tetrahydrofuran. The crude product precipitated as a white solid as the liquid cooled to room temperature. Recrystallization from 4 mL of fresh tetrahydrofuran produced 4.1 g (80% yield) of the N,N' bis (2-lauramidoethyl) ethylenediamine, mp. 110-112°C. The ¹H and ¹³C NMR, DEPT¹³C NMR, IR and Mass Spectra were recorded and agreed with the proposed structure.

EXAMPLE 3

Synthesis of the N,N'-bis(2-lauramidoethyl) ethylenediamine-N,N' di(sodium propionate), compound of Formula V wherein R1 is C11H23.

To a 250 mL three-necked, round bottom flask equipped with a magnetic stirring bar, temperature control, and a condenser was added 5.9 g (10 mmol) of N,N'-bis(2-lauramidoethyl) ethylenediamine of Example 2 (greater than 98% purity) and 8.6 g (100 mmol) of methyl acrylate. The reaction mixture was then refluxed at 80°C for 13 hours with stirring. After stripping out excess methyl acrylate under vacuum, 6.35 g (100% yield) of white waxy solid product was obtained. Gas chromatography showed that the waxy solid contained more than 98% of the desired di-(methyl ester) of the title compound which was characterized by ¹H and ¹³C NMR.

To another 250 mL, three necked, round bottom flask equipped with a magnetic stirrer bar and temperature control, was added 0.7 g NaOH in 23 mL of water. The reaction mixture was heated to 45° to 55°C. At this temperature, 5.6 g of the white, waxy dimethyl ester product obtained above was added in one portion. The reaction mixture was stirred at 45° to 55°C for 5 to 6 hours.

After completion of the hydrolysis, the contents were transferred to a beaker which was then placed in a heated water bath. Evaporation of the water left 5.7 grams of the amphoteric surfactant of the title compound, Formula V, as a white solid. The ¹H and ¹³C NMR were recorded and agreed with the proposed structure.

EXAMPLE 4

Synthesis of N,N' bis(2-lauramidoethyl) ethylenediamine-N,N' di(sodium acetate) compound of Formula IV wherein R1 is C11H13.

To a 500 mL three-necked, round bottom flask equipped with a mechanical stirrer bar, thermometer and a condenser, 28.4 g (300 mmol) of monochloroacetic acid and 200 mL of water were added. The stirred solution was cooled in an ice bath during the dropwise addition of 26.2 g (300 mmol) 50% NaOH to maintain the temperature below 25°C. The ice bath was removed, and 61.5 g (100 mmol) of bisamidoamine of Formula X prepared according to Example 2 and 50 g of isopropyl alcohol was added and the liquor was heated to 75°C. The pH was maintained at 9-10.5 by addition of 21.8 g (270 mmol) 50% NaOH at 75°C over the 5 hour reaction period. The reaction mixture was then heated to 85°C and 42 mL of IPA/water was distilled out and replaced with 42 mL of water. The reaction was run another 12 hours at 90°C, until the reaction was complete as indicated by the free to total chloride ratio of near unity (>.99 - 99% conversion).

The solvent was allowed to evaporate overnight in a crystallizing dish in the hood. Drying was completed in a vacuum oven at 70°C for 2 hours, to give 74 g of the desired product. (81% of theoretical) The structure was confirmed by the ¹³C NMR spectrum.

EXAMPLE 5

Synthesis of N,N' bis(2-lauramidoethyl) ethylenediamine-N,N'-di(sodium 2-hydroxy-3 propyl sulfonate) compound of Formula VI wherein R1 is C11H23.

To a 250 mL, three-necked, round-bottom flask equipped with a mechanical stirrer bar thermometer and a condenser, were added 5.7 g (60 mmol) of sodium metabisulfite, 60 mg of 50% NaOH and 33.9 g of water. The reaction mixture was heated to 50-60°C and epichlorohydrin (5.55 g, 60 mmol) was added over a period of about an hour. The reaction mixture was then heated with stirring at 60-65°C for one hour, after which 10.3 g (20 mmol) of the bisamidoamine compound of Formula X prepared according to the process of Example 2, 12 g of isopropyl alcohol and 44 g of water were added. The reaction mixture was heated to reflux, and 4.8 g (60 mmol) of 50% NaOH was added over a period of 3 hours.

About 6 mL of alcohol/water was then distilled out and replaced with 8 mL of water. After heating to reflux for two hours, another 10 mL of water was added and reflux continued for another hour.

The product was evaporated to dryness, extracted with tetrahydrofuran, and the solvent evaporated. Yield: 15 g, 60% yield. Structure confirmed by ¹³C NMR.

EXAMPLE 6

Synthesis of N,N'-bis(2-caprylamidoethyl)ethylenediamine-N,N'-di(sodium propionate) compound of Formula V wherein R₁ is C₇H₁₅.

Preparation of the bisimidazoline compound of Formula VIII wherein R₁ is C₇H₁₅.

The procedure of Example 1 was repeated using 100 g (0.538 mol) of triethylenetetramine hydrate, 154.9 g (1.076 mol) of octanoic acid and 100 mL of toluene.

Preparation of bisamidoamine compound of Formula X wherein R₁ is C₇H₁₅.

The procedure of Example 2 was followed using a 500 mL, 3-necked round bottom flask, 145 grams (0.4 mol) of bisimidazoline as prepared above, 4 g of 50% NaOH and 4 mL of water. Reaction time was 4 hours. The product was recrystallized from 80 mL of tetrahydrofuran and 200 mL water. The yield was 80 grams (42% yield) and the structure was confirmed by ¹³C NMR.

Synthesis of amphoteric surfactant compound of Formula V wherein R₁ is C₇H₁₅

To a 500 mL, four-necked, round bottom flask equipped with a mechanical stirrer, thermometer and condenser was added 64.0 g (0.16 moles) bisamidoamine as prepared above and 62 g of toluene and heated to 75-85°C.

Methyl acrylate (55.4 g, 0.64 mol) was added dropwise over a period of one hour. The reaction temperature was maintained at 80-85°C for 16 hours. Excess toluene and methyl acrylate were stripped. ¹³C NMR confirmed the desired structure with a product purity of about 90%.

To this crude mixture was added 360 mL of water and 11.2 g (0.14 moles) of 50% NaOH and heated to 93-97°C. Another 11.2 g (0.14 moles) of 50% NaOH was added incrementally to maintain the pH at 9.0-10.0. Total reaction time was six hours. The reaction mixture was placed in an evaporating dish and evaporated to dryness at 60-80°C. and finished in a vacuum oven. The product was extracted in a Soxhlet extractor with tetrahydrofuran for four hours. The product was allowed to air dry to remove tetrahydrofuran, and drying was completed in vacuum oven. Yield 45.5 g, 49.2% yield. The structure was confirmed by ¹³C NMR.

SURFACE PROPERTIES

The surfactants of the invention were measured for critical micelle concentration and their ability to reduce surface tension.

The test methods utilized are described as follows:

Critical Micelle Concentration (CMC)

Aqueous solutions of a surfactant were prepared at varying concentrations. The surface tension at 20°C was measured by the Wilhelmy plate method and plotted vs. the logarithm of the concentration. The critical micelle concentration was determined as the value at which the slope of the line changed abruptly.

Surface Tension Reducing Ability (gamma CMC)

The surface tension reducing ability was determined from the surface tension at the critical micelle concentration.

Surface tension measurements were made for each of the referenced surfactants, using a Kruss K-12 Tensiometer (plate method). Each experiment was carried out as follows.

Distilled water solutions at different concentrations were prepared for each of the test surfactants in 100 mL amounts. The mixtures were stirred until homogeneous solutions were obtained. The surface tensions of these solutions were then measured.

From the surface tension data, the area/molecule (area) at the interface and efficiency of adsorption were computed by use of the appropriate Gibb's Adsorption Equation:

$$\rho = \frac{-dy}{d \log C_T} / 2.303 RT$$

where

ρ = surfac excess concentration (mol/cm²)

dy = change in surface or interfacial tension of the solvent (dyn·cm⁻¹)

R = 8.31 × 10⁷ erg mol⁻¹ °K⁻¹

C = molar concentration of solution

T = absolute temperature (°K)

pC-20 at the solution /air interface is defined as the negative logarithm of the surfactant concentration required to lower surface tension by 20 dyne/cm.

The results obtained for the surfactants alone are reported in Table 1.

TABLE 1

SURFACE ACTIVITY					
Surfactant	CMC (M)	γ_{cmc}	AREA (\AA^2)	pC-20	
Product of EXAMPLE 3 (C12 PROPIONATE) pH 9.5, 0.1 M NaCl	6.3×10^{-7}	34.0	56	7.3	
Product of EXAMPLE 5 (C12 SULPHONATE) pH 7.0, 0.1 M NaCl	3.5×10^{-6}	29.5	53	6.7	
CONTROL MIRANOL® H2M-SF (Lauroamphodipropionate) pH 9.5, 0.1 M NaCl	4.7×10^{-5}	33.5	63	5.6	
CONTROL MIRANOL® ULTRA (Cocoamphoacetate) pH 6, 0.1 M NaCl	2.0×10^{-4}	26.5	63	5.4	
CONTROL RHODAPEX® ESY (Lauryl Ether Sulfate) pH 6, 0.1 M NaCl	8.0×10^{-5}	30.2	42	5.0	
CONTROL MIRANOL® CS (Cocoamphohydroxypropyl sulphonate) pH 7, 0.1 M NaCl	5.6×10^{-5}	27.0	58	5.8	

HYDROTROPICITY

Hydrotropicity was measured by determining the amount of surfactant needed to clarify a cloudy aqueous solution of 5% sodium hydroxide and 5% surfactant (IGEPAL® CO-630 - Nonylphenol ethoxylate - 9 moles EO). The results are expressed in weight percent of the aqueous solution. The lower the number, the greater the hydrotropicity. The results show that the product of Example 6 is over 60% more efficient than the conventional surfactant MIRANOL® JEM.

TABLE 2

SURFACTANT	HYDROTROPICITY (Wt. %)
Product of EXAMPLE 6 (C ₈ PROPIONATE)	0.3 %
MIRANOL® JEM (Sodium Mixed C ₈ Amphocarboxylate)	0.8 %

When the surface properties for the amphoteric C₁₂ propionate and C₁₂ sulfonate compounds of the invention are compared to the corresponding conventional amphoteric laurylamphopropionate and cocoamphosulfonate as shown in Table 1, the novel compounds of the invention show two unexpected surface active properties; unusually low critical micelle concentration (CMC) and pC-20 values in aqueous media. These properties are a measure of the tendency of the surfactant to form micelles, and adsorb at the interface, and consequently, to reduce surface tension, respectively. The values shown in Table 1 demonstrate that the C₁₂ propionates and sulfonates are one to two orders of magnitude (or 10 to 100 times) more efficient at reducing surface tension (pC-20) and more than two orders of magnitude (or 100 times) more effective at forming micelles. This unusually high surface activity for these molecules is a result of their unique structure; the presence of two optimally spaced hydrophobic moieties and hydrophilic groups. This molecular structure provides energetically favorable decreases in the free energy of adsorption and micellization through favorable distortion of the water structure, while simultaneously, providing a "closed packed" arrangement at the interface as reflected by the unusually low area per molecule compared to that which would be expected from the molecular dimensions. The area per molecule for the compounds of the invention are less than that of conventional amphoteric having single hydrophilic chains and hydrophobic moieties, based on similar starting materials and about half the molecular weight. The ability of the compounds of the invention to distort water structure through inhibition of crystalline or liquid crystalline phase formation in the bulk phase and at the same time to pack closely on adsorption at the interface is contrary to conventional wisdom. This again demonstrates the uniqueness of the molecular design for these compounds which is very critical to providing, unexpected, exceptional surface and performance properties.

Exceptional surface activity and unique structural features for the compounds of the invention provide two other important performance properties that can have immense practical application in industry. They are hydrotropicity, which is the ability of organic substances to increase the solubility of other, insoluble organic substances in water, and solubilization, the dissolving of water insoluble organic compounds into aqueous surfactant solutions above their critical

micelle concentrations. The compounds of the invention, because of their very low CMC values, are efficient solubilizers. This latter property will not only allow the formulation of homogeneous water insoluble materials, but also will enhance the surface activity of other surfactants whose low water solubility restricts their use. These novel surfactants of the invention are far better than comparable conventional surfactants in hydrotropic and solubilizing properties.

Because of their unusually high surface activity coupled with their hydrotropicity and solubilization properties, compounds of this invention will provide exceptionally high performance properties, at very low concentration, in practical applications such as detergency emulsification, solubilization, dispersancy, hydrotropicity, foaming and wetting. Because of their greater surfactant efficiency as indicated by the extremely low CMC and pC-20 values, from ten to 100 times lower concentrations of the compounds of the invention can be used compared to the invention than conventional surfactants, substantially reducing the need for the surfactant component to achieve equivalent results and thus reducing the amount of surfactant released into waste treatment facilities. Additionally, since the CMC is the maximum free surfactant concentration (that is, uncomplexed in micelles) under use conditions, this lower level of the active species should result in a much lower level of irritancy, even essentially none, if as is likely, it is below the irritancy threshold concentration.

SURFACE ACTIVITIES OF MIXTURES

The unusually high surface activity of the amphoteric surface active agents of the invention make them the surfactants of choice in enhancing the surface activity of mixtures containing other conventional significantly less surface active zwitterionic, amphoteric, nonionic and cationic surfactants. The propionate and sulfonate compounds of the invention provide significant, unexpected improvement in the surface activity of blends of these compounds with the above types of surfactants, even when used in very small amounts. The improvement is beyond that which would be estimated from an average of the properties of the components of the surfactant mixture, hence showing positive synergism. The results are shown in Table 3 as follows:

TABLE 3

SURFACE ACTIVITIES of MIXTURES

PRODUCT OF EXAMPLE 3 (C ₁₂ propionate) pH 7, 0.1 M NaCl	CMC (M)	γ_{cmc}	area (Å ²)	pC-20
PLUS MIRANOL® ULTRA (Cocoamphoacetate) (25/75 mole ratio)	7.9×10^{-6}	27	40	6.1
PLUS RHODAPEX® ESY Lauryl ether Sulfate - 1EO) (25/75 mole ratio)	4.8×10^{-6}	26	75	7.1*
PLUS MIRANOL® H2M-SF (Lauroamphodipropionate) (25/75 mole ratio) pH 9.5	2×10^{-6}	32	47	6.6
CONTROL				
RHODAPEX® ESY/MIRANOL® ULTRA (25/75 mole ratio) pH 6	6.5×10^{-5}	25	42	5.3

(*Extrapolated)

As shown in Table 3, the compound of Example 3 (C₁₂ propionate) when blended with coco amphoacetate, or the lauryl amphodipropionate comparable conventional amphoterics, at 25/75 molar ratios provided at least a 10 fold improvement in surface activity, as measured by the reduction of CMC and pC-20 compared to the conventional amphoterics alone. Similar order of magnitude improvement in surface activity was obtained for a blend of the compound of Example 3 (C₁₂ propionate) with a conventional anionic surfactant, lauryl ethersulfate (RHODAPEX® ESY) at the 25/75

molar ratio. This enhancement of surface activity (CMC AND pC-20) is also one to two orders of magnitude greater than for a mixture of corresponding conventional surfactants, i.e., RHODAPEX® ESY and MIRANOL® ULTRA. This property of enhancement of surface activity and solubilization of blends when used in low concentrations can have wide applicability in industrial, personal care and pharmaceutical applications. The use of the compounds of the invention in combination with conventional surfactants can provide improved performance for blends even at significantly lower concentrations which is very desirable for both economic and environmental reasons.

The product of the invention was evaluated for mildness by an In-Vitro Ocular Irritation (Eytex) study. The product of Example 3 gave an Eytex Draize Equivalent of 9.7. This corresponds to minimal irritation.

The product of Example 3 was also tested in combination with RHODAPEX® ESY. The results indicate that the irritancy of RHODAPEX® ESY was reduced from moderate irritant to minimal/mild when combined with the product of Example 3.

Eytex Draize Equivalent (EDE)

0-15 Minimal
15-19 Minimal/Mild
19-22 Mild
2-25 Mild/Moderate
25-33 Moderate

TABLE 4

<u>Eytex Draize Equivalent (EDE)</u>		
AMOUNT	SAMPLE IDENTIFICATION	EDE
10.0%	Product Example 3	9.7
2.5%	Product Example 3	21.8
7.5%	RHODAPEX® ESY	
5.0%	Product Example 3	19.6
5.0%	RHODAPEX® ESY	
7.5%	Product Example 3	18.5
2.5%	RHODAPEX® ESY	
10.0%	RHODAPEX® ESY	27.1

By virtue of the properties discussed above, the surfactants of the invention can be combined with other, conventional surfactants in very small amounts to dramatically improve surface activity, and solubility of blends and, thereby, have wide industrial applicability in significantly improving performance properties such as detergency, emulsification, wetting, dispersancy and solubilization. Further, this property of significantly lowering CMC and pC-20 values in mixtures containing conventional surfactants should provide irritancy mitigating properties when used in combination with other more irritating surfactants, polymers and/or additives.

Mixtures were evaluated for improvement in foam height and wetting ability. Blends of the compounds of the invention with some conventional surfactants showed significant improvement as shown using the following tests.

Ross Miles Foam Height

The product was evaluated as a foaming agent using the Ross Miles Foam Height Test as outlined in ASTM method D1173. The foam was evaluated and the results were recorded.

DRAVES WETTING TEST

The Draves Wetting Test is conducted according to ASTM D 2281-68. A 500 mL surfactant solution containing 0.1 % by weight of the test surfactant was prepared. The resulting aqueous solution was poured into 500 mL graduate cylinder and 5 g of 100% cotton yarn weighted with 3 g hook was dropped into the cylinder. The time required for the

yarn to sink to the bottom of cylinder was reported as Drave Wetting Time.

The following results were obtained:

TABLE 5

<u>Ross Miles Foam Height</u>	
Product of EXAMPLE 3 (C ₁₂ Propionate) 0.1 wt% Sol., pH 7	Ross Miles Foam Height (mm, 0 to 5 min.)
BLENDING WITH MIRANOL® H2M-SF WT. RATIO	
100/0	117 --> 106
75/25	123 --> 123
50/50	136 --> 136
25/75	145 --> 145
0/100	133 --> 133

TABLE 6

<u>Draves Wetting Time</u>	
Product of EXAMPLE 3 (C ₁₂ Propionate) 0.1 wt% Sol., pH 7	Draves Wetting Time (sec)
BLENDING WITH MIRANOL® H2M-SF WT. RATIO	
100/0	>300
75/25	133
50/50	116
25/75	81
0/100	140

TABLE 7

<u>Draves Wetting Time</u>	
Product of EXAMPLE 3 (C ₁₂ Propionate) 0.1 wt% Sol., pH 7	Draves Wetting Time (sec)
BLENDING WITH IGEPAL® CO-430 WT. RATIO	
66/36	36.2
46/54	26.0
37/63	33.5
0/100	>300

As used herein RHODAPEX® ESY is a sodium lauryl ether sulfate (1 EO); MIRANOL® H2M-SF is a salt free disodium lauroamphodipropionate; MIRANOL® CS is a sodium cocoamphohydroxypropyl sulphonate of the formula (Coco)-C(O)NHCH₂CH₂N(CH₂CH₂OH)CH₂CH(OH)CH₂SO₃Na; and MIRANOL® ULTRA is a cocoamphoacetate of the formula (Coco)-C(O)NHCH₂CH₂N(CH₂CH₂OH)CH₂CO₂Na.

MIRANOL® CS, MIRANOL® H2M-SF, MIRANOL® JEM AND MIRANOL® ULTRA are amphoteric surfactants and RHODAPEX® ESY is an anionic surfactant. These materials are available from Rhône-Poulenc Specialty Chemicals Co.

Although the subject invention has been described with respect to a preferred embodiment, it will be readily apparent to those skilled in the art to which the invention pertains that changes and modifications may be made thereto without departing from the spirit or scope of the subject invention as defined by the appended claims.

Claims

1. A surfactant comprising compounds of the formula:

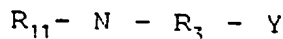
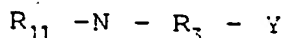


I.

 R_4 

wherein R_1 can independently be C_5 to about C_{22} alkyl or hydroxy substituted or perfluorinated derivatives thereof, R_2 can independently be C_1 to about C_{12} alkylene or hydroxy substituted alkylene; B can be an amide group $[-C(O)N(R_5)-$ or $-N(R_5)C(O)-]$, a carboxyl group $[-C(O)-O-$ or $-OC(O)-]$ or a polyether group $[-(O(R_6-O))_x-]$, wherein R_5 independently represents lower alkyl or hydroxy substituted alkyl of 1 to 4 carbons or hydrogen and R_6 independently represents about C_2 to about C_4 alkyl with x being a number between 1 and 20; R_3 can independently be C_1 to about C_{10} alkylene and the hydroxy substituted derivatives thereof or R_7-D-R_7 or a polyether group $[-(O(R_6-O))_x]$ wherein R_6 is as defined hereinbefore and R_7 can independently be C_1 to about C_6 alkylene and the hydroxy substituted derivatives thereof and D represents $-O-$, $-S-$ or $-N(R_8)-$ wherein R_8 independently represents C_1 to about C_{12} alkyl and the hydroxy substituted derivatives thereof or hydrogen; R_4 can independently be alkylene or alkylaryl of 1 to about 10 carbon atoms and the hydroxy substituted derivatives thereof or $R_9 - D_1 - R_9$ wherein R_9 can independently be alkylene of from 1 to about 6 carbon atoms and the hydroxy substituted derivatives thereof as well as aryl, and D_1 represents $-O-$, $-S-$, $-SO_2-$, a carbonyl group, a polyether group $[-(O(R_7-O))_x-]$, $-(R_{10})_y[N(R_{10})]_z-$ or aryl wherein R_{10} represents alkyl of from 1 to about 12 carbon atoms and the hydroxy substituted derivatives thereof or hydrogen, R_7 being as defined hereinbefore with x being a number between 1 and 20 and y and z are independently numbers from 1 to about 4; and Y independently represents $-SO_3H$, $-OSO_3H$, $-OP(O)(OH)_2$, $-P(O)(OH)_2$, $-COOH$, $-CO_2-C_6H_4-SO_3H$ and salts thereof.

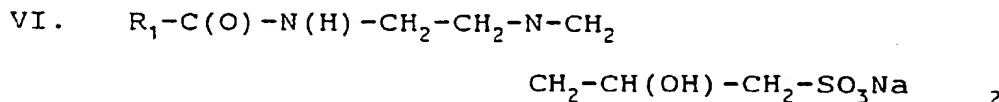
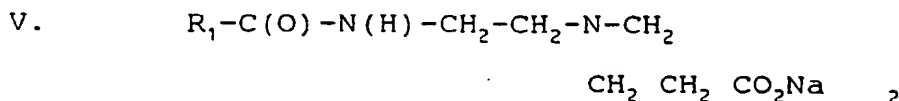
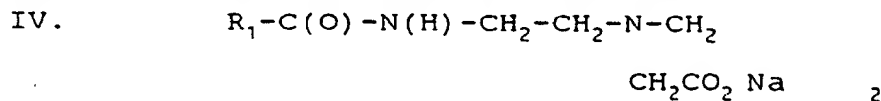
2. The surfactant of Claim 1, wherein R_1 is alkyl of from about C_6 to about C_{18} carbon atoms.
3. The surfactant of Claim 1, wherein R_2 is alkylene of from about C_2 to about C_6 carbon atoms.
4. The surfactant of Claim 1, wherein B is an amide group.
5. The surfactant of Claim 1, wherein R_3 independently is lower alkylene of from 1 to about 4 carbon atoms.
6. The surfactant of Claim 1, wherein R_4 is lower alkylene of from 1 to about 10 carbon atoms.
7. The surfactant of Claim 1, wherein Y is sulfate, carboxylate, phosphate and salts thereof.
8. The surfactant of claim 1, wherein said salt in Formula I is selected from the group consisting of an alkali metal salt, an alkaline earth metal salt, an ammonium salt, and an organic base salt.
9. The surfactant of claim 1, wherein said organic base salt is selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine, triethylamine, trimethylamine and N-hydroxyethyl morpholine.
10. The surfactant of claim 1, wherein said salt in Formula I is an alkali metal salt.
11. A blend of surfactants comprising a surfactant of the formula:

 R_2 

wherein R_{11} can independently be alkyl or hydroxy alkyl of from 6 to 22 carbons or $R_1 - B - R_2$ wherein R_1 , R_2 , R_3 , and R_4 are as defined hereinbefore and at least one surfactant selected from the group consisting of an anionic,

nonionic, cationic, or amphoteric surfactant.

12. The blend of surfactants of claim 11, wherein said nonionic surfactant is selected from the group consisting of a fatty acid glycerine ester, a sorbitan fatty acid ester, a sucrose fatty acid ester, a polyglycerine fatty acid ester, a higher alcohol ethylene oxide adduct, a single long chain polyoxyethylene alkyl ether, a polyoxyethylene alkyl allyl ether, a polyoxyethylene lanolin alcohol, a polyoxyethylene fatty acid ester, a polyoxyethylene glycerine fatty acid, a polyoxyethylene propylene glycol fatty acid ester, a polyoxyethylene sorbitol fatty acid ester, a polyoxyethylene castor oil or hardened castor oil derivative, a polyoxyethylene lanolin derivative, a polyoxyethylene fatty acid amide, a polyoxyethylene alkyl amine, an alkyl pyrrolidone, glucamides, alkylpolyglucosides, a mono or dialkanol amide, a polyoxyethylene alcohol mono or diamide, and an alkylamine oxide.
13. The blend of surfactants of claim 11, wherein said anionic surfactant is selected from the group consisting of a fatty acid soap, an ether carboxylic acid and salt thereof, an alkane sulfonate salt, an α -olefin sulfonate salt, a sulfonate salt of a higher fatty acid ester, a higher alcohol sulfate ester salt, fatty alcohol ether sulfate salts, a higher alcohol phosphate ester salt, a fatty alcohol ether phosphate ester salt, a condensate of higher fatty acids and amino acids, and a collagen hydrolysate derivative.
14. The blend of surfactants of claim 11, wherein said cationic surfactant is selected from the group consisting of an alkyltrimethylammonium salt, a dialkyl-dimethylammonium salt, an alkyldimethylbenzylammonium salt, an alkylpyridinium salt, an alkylisoquinolinium salt, benzethonium chloride, and an acylamino acid type cationic surfactant.
15. The blend of surfactants of claim 11, wherein said amphoteric surfactant is selected from the group consisting of an amino acid, betaine, sultaine, phosphobetaine, an imidazoline type amphoteric surfactant, soybean phospholipid, and yolk lecithin.
16. The surfactant of claim 1, further comprising an auxiliary additive.
17. The surfactant of claim 16, wherein said auxiliary additive is selected from the group consisting of an inorganic salt such as Glauber salt and common salt, a builder, a humectant, a solubilizing agent, a UV absorber, a softener, a chelating agent, and a viscosity modifier.
18. The surfactant of claim 1, wherein said compound of formula (I) is selected from the group consisting of -



wherein R_1 is as defined hereinbefore.

19. A cleaning composition comprising an aqueous solution having a cleaningly effective amount of the composition of Claim 1 dissolved therein.
20. The cleaning composition of claim 19, wherein the solution is selected from the group consisting of hair shampoos, baby shampoos, body shampoos, bubble baths, bar soaps, bath gels, hair conditioning gels, skin creams and lotions, skin contacting cosmetics, make up removal creams and lotions, liquid detergents, dish detergents, liquid soaps, bleach activators, bleach stabilizers and the like.

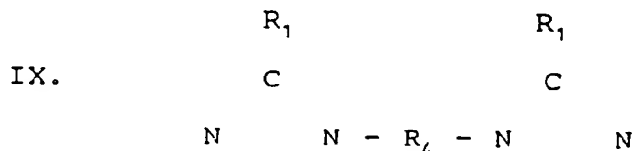
21. The cleaning composition of claim 19, wherein the solution is selected from the group consisting of hard surface cleaners, emulsion polynization, laundry and dish detergent, liquid and bar soap, carpet cleaners, lubricants, metal cleaners and textile processing acids.

22. A process for preparing the compounds as recited in claim 1 which comprises:

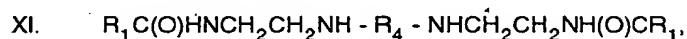
a. reacting a polyamine of the formula



wherein R_4 is alkyl or aminoalkyl with a fatty acid or ester or triglyceride thereof to form a bisimidazoline of the formula



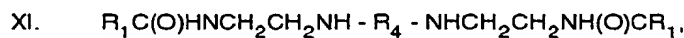
b. hydrolyzing the bisimidazoline to form a bisamidoamine of the formula



and

c. alkylating the bisamidoamine to form the compound of claim 1.

23. A bisamidoamine compound of the formula



and

wherein R_1 can independently be C_6 to about C_{22} alkyl or hydroxy substituted or perfluorinated derivatives thereof, and R_4 represents alkyl, hydroxy-substituted alkyl, alkylaminoalkyl, an ether or an alkylarylalkyl linkage.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 40 1881

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 344 334 (WACKER-CHIMIE) * page 3, line 39 - line 46; claim 1 *	1-3, 5-13, 19, 21	B01F17/00 C11D1/88 A61K7/50
X	DATABASE WPI Section Ch, Week 9523 Derwent Publications Ltd., London, GB; Class A97, AN 95-176476 & RO-B-108 563 (SC VERACHIM SA), 30 June 1994 * abstract *	23	
A	EP-A-0 373 491 (HENKEL) * page 3, line 1 - line 16 * * page 3, line 47 - line 50 *	19, 20, 22	
A	EP-A-0 319 942 (BEREUTER) * claims 1, 7 *	1, 2, 5-8, 10, 18	
A	US-A-5 160 450 (MITSUO OKAHARA) * the whole document *	11-17	
A	EP-A-0 543 432 (BEROL NOBEL) * claim 1 *	19-21	
A	US-A-3 898 244 (R.B. MCCONNELL) * column 2, line 13 - line 16; claim 1 *	1-3, 5-7, 11	
A	US-A-4 269 730 (J.R. WECHSLER) -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 4 December 1995	Examiner Hilgenga, K
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 (11/91) (PMD/11)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 95/00767

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C233/36 C07C233/38 C11D1/52 C07C233/18 C07C233/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

27 April 1995

Date of mailing of the international search report

11.05.95

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Seufert, G

Int. l. Application No
PCT/US 95/00767

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 107, no. 22, 30 November 1987, Columbus, Ohio, US; abstract no. 200335, L. M. BADOIU ET AL. 'Textile softeners based on alkoxyethyl derivatives of fatty amides' page 100 ; see RN 68310-20-3, Poly(oxy-1,2-ethanediyl), .alpha..alpha.'-[[[(1-oxooctadecyl)imino] bis[2,1-ethanediyl][(1-oxooctadecyl)imino]- 2,1- ethanediyl]]bis[.omega.-hydroxy-	1-7
X	see RN 111233-77-3, Octadecanamide, N,N'-(iminodi-2,1-ethanediyl)bis[N-(hydroxymethy l)]-	1,3,5-7
X	see RN 111172-25-9, Poly(oxy-1,2-ethanediyl), .alpha..alpha.'-[iminobis[2,1- ethanediyl [(1-oxooctadecyl)imino]methylene]]bis[.ome ga.- (hexadecyloxy)-	1,3,5-7
X	see RN 68310-19-0, Poly(oxy-1,2-ethanediyl), .alpha.-hydro-.omega.-hydroxy-, ether with N,N'-[[[(2-hydroxyethyl)imino]di-2,1-ethane diyl]bis[N-(2- hydroxyethyl)octadecanamide] (3:1) & RO,A,89 940 (INTREPRINDEREA DE DETERGENTI) 12 March 1984	1
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INTERNATIONAL SEARCH REPORT

...information on patent family members

International Application No

PCT/US 95/00767

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EP-A-0258500	09-03-88	EP-A, B 0258923 JP-A- 63068699 US-A- 4851138	09-03-88 28-03-88 25-07-89